Studies on the Oxide Magnets. I : Effects of Bi_20_3 on Barium Ferrites

Studies on the Oxide Magnets. I
Effects of Bi_2O_3 on Barium Ferrites

Tosihiko OKAMURA, deceased.
Hiroshi KOJIMA and *Seiichiro WATANABE
Research Institute for Scientific Measurements

(Received February 22, 1955)

Synopsis

Magnetic properties of Ba-ferrites with and without Bi_2O_3 were compared. Cylindrical specimens were prepared from $BaCO_3$ and Bi_2O_3, and Fe_2O_3 from $Fe(CO)_5$. The first reaction was performed at 900°C for 2 hours, and then sintered at 1100°~1200°C for 15 minutes.

The magnetic and mechanical properties of Ba-ferrite, were improved by the addition of Bi_2O_3 under the condition in which sintering was performed, especially at the composition $Fe_2O_3/BaO<6$. And it was considered that the effects might be due to the densification of specimens, and not to the ferromagnetic new phase of BaO-Bi_2O_3-Fe_2O_3 system.

I. Introduction

The ferromagnetic properties of $PbO{\cdot}6Fe_2O_3$ which was called magneto-plumbite, were reported in the earlier period of this century. But through the recent invention in the Netherlands of the sintered oxide magnet, $BaO{\cdot}6Fe_2O_3$,[1][2] which has the same crystal structure as the mineral, the magnet of this type has become an object of study for the first time for industrial use.

However, there has been no report made on the improvement of the magnet by an addition of other elements[3]. That is to say, it has been found that the sintered magnets of BaO, PbO or SrO, etc. and $6Fe_2O_3$ have very high coercive force under suitable sintering conditions, but that their properties—mainly their remanent which is the object of the present research—could scarcely be improved by the addition of other elements. In other words, it has been found that the oxide magnets are very stable against impurities and it is easy to produce the magnets on an indurstrial scale.

Intrinsic coercive force, ${}_iH_c$, of some oxide magnets of this type in market is over 4000 oersted, but their remanent, $4\pi I_r$, is about 2300 gauss at most. It is desirable, therefore, to increase the remanent by some method for industrial use of

---

* Nihon Tokushyu Ko K.K. (Japan Special Steel Co.) Tokyo.

(1) J. J. Went, G. W. Rathenau, E. W. Gorter, Gorter, G. W. v. Oosterhout, Philips Techn. Rev. **13** (1952), 194.
Phys. Rev., **86** (1952), 424.
Japanese Pat. (Notification No. 5734) 1954.

(2) G. W. Rathenan, Rev. Mod. Phys., **25** (1953), 297.

(3) A paper almost of the same contents was read by Dr. T. Takei at the 50th Annual Meeting of Sci. Res. Inst. (Oct. 7, 1954 at Tokyo), and we found the abstracts in the Rep. Sci. Res. Inst. Vol. 30 No. 6 (1954). after the completion of the present work.

the magnets. The authors carried out the experiments on the effects of additional elements on the magnetic properties of oxide magnets, and results obtained will be published successively.

The effects of Bi_2O_3 on BaO-Fe_2O_3 system will be given in this paper.

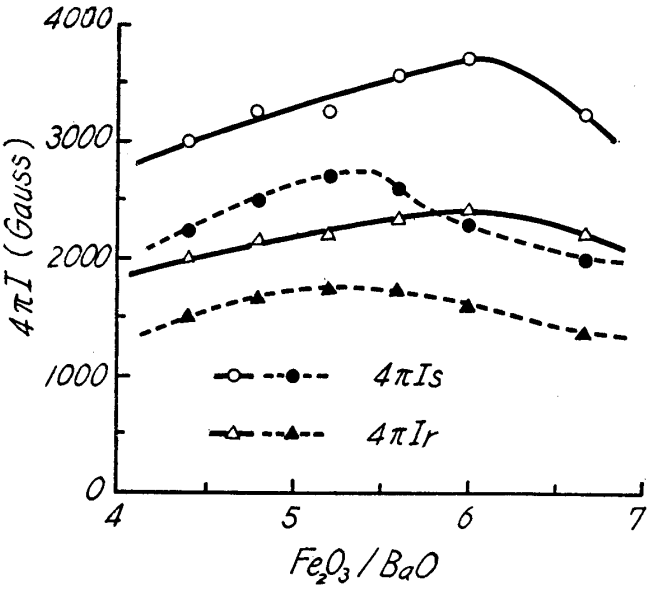

Fig. 1. Saturation and remanent as a function of Fe_2O_3/BaO for the specimens sintered at 1100°C for 15 minutes.
Solid line : $Bi_2O_3=1.5\%$
Brrken line : $Bi_2O_3=0\%$

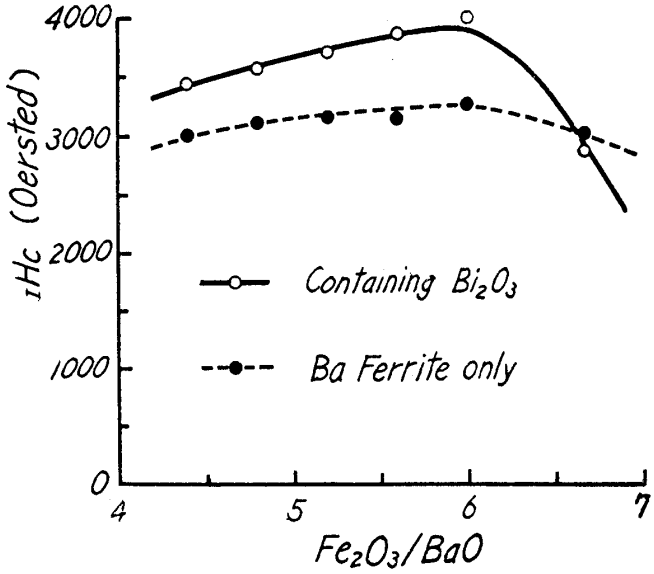

Fig. 2. Coercive force as a function of Fe_2O_3/BaO for the specimens sintered at 1100°C for 15 minutes.
Solid line : $Bi_2O_3=1.5\%$
Broken line : $Bi_2O_3=0\%$

II. Experimental procedure

The magnetic properties of the oxide magnets in these systems are very sensitive to sintering condition. If they are sintered at the temperature 50°C higher than the proper temperature, the remanent and the corecive force will decrease abruptly. And the suitable sintering condition greatly depends upon the activity of oxide powder as raw materials. So, the properties of oxide powder must be kept as constant as possible in order to study the effects of additional elements. From this point of view, Fe_2O_3, which constitutes the greater part of the oxide magnet, was prepared by the oxidation of $Fe(CO)_5$. The producing method and properties of the hematite powder were already reported by one of the authors[4].

As materials for Ba and Bi, the first grade chemical reagents of $BaCO_3$ and Bi_2O_3 were provided by a certain manufacturer.

After drying, these powders were mixed by a mechanical mixer for about 30 minutes at a certain mol ratio. Then, the powder was heated in a Tammann tube in an electric furnace. After cooling, the powder was ground again, and weighing about 4.5 gr, it was

(4) H. Kojima, Rep. of Res. Inst. Sci. Meas., Tohoku Univ. **2** (1952), 101 ; Chem. Engineer's Digest **20** (1952), 225.

pressed into a cylindrical form 10 mm in diameter with a pressure of 6 ton/cm^2. The specimen was sintered in the air under a certain sintering condition.

The magnetic hysteresis loop of the specimen was observed by an electromagnet and a ballistic galvanometer, and the maximum measuring field was about 10000 oersted. The density of specimens after sintering was different with their composition and with sintering conditions, etc., rangeing from 3.5 to 5.1.

III. Experimental results

Magnetic properties were measured with the specimens which were heated at 900°C for 2 hours and sintered for 15 minutes at 1100°, 1150° and 1200°C respectively. Changing the ratio of Fe_2O_3/BaO from 4.4 to 6.6, the magnetic properties of single barium ferrites and barium ferrites mixed with Bi_2O_3 were compared, as shown in Figs. 1~6. That is, Figs. 1, 3 and 5 show the magnetic saturation $4\pi I_s$ and remanent $4\pi I_r$ of barium ferrites with and without 1.5% Bi_2O_3, sintered at 1100°, 1150° and 1200°C respectively.

Fig. 2, 4 and 6 illustrate the intrinsic coercive force ${}_iH_c$ of the same specimens, corresponding to the above figures. In these figures, solid lines show the magnetic properties of the specimens with Bi_2O_3 (called *M*-system in the paper) and dotted lines show those of the specimens without Bi_2O_3 (called *S*-system). The maximum point of $4\pi I_s$ in *S*-system is about 5.5 in the value of Fe_2O_3/BaO (called *P*), and the saturation value decreases abruptly from $P = 6.0$, as is shown in Fig. 1. The remanent curves run almost parallel with the saturation curves. As for *M*-system containing Bi_2O_3 1.5 mol%, $4\pi I_r$ and $4\pi I_s$ are

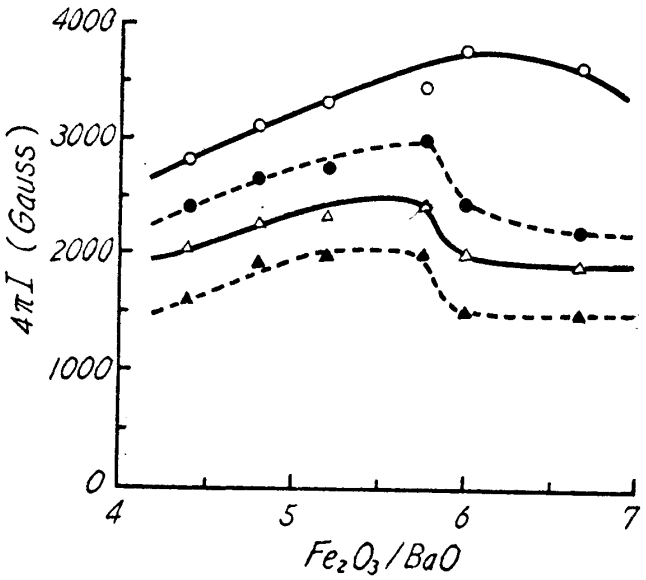

Fig. 3. Saturation and remanent as a function of Fe_2O_3/BaO for the specimens sintered at 1150°C for 15 minutes.
Solid line : Bi_2O_3=1.5%
Broken line : Bi_2O_3=0%

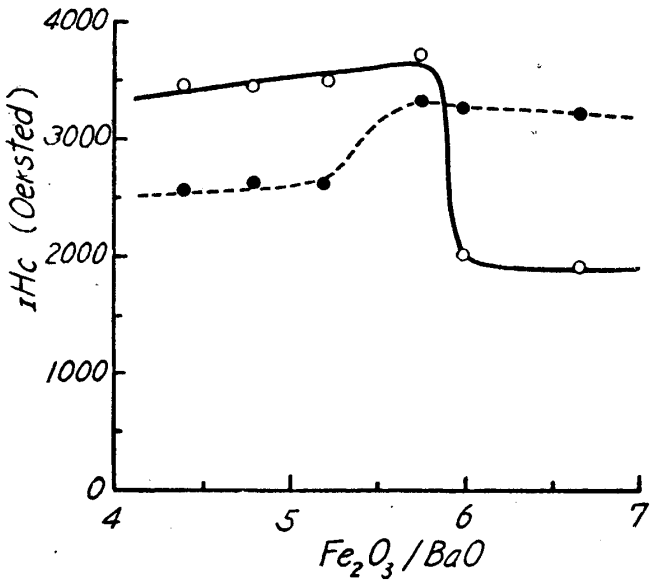

Fig. 4. Coepcive force as a function of Fe_2O_3/BaO for the specimens sintered at 1150°C for 15 minutes.
Solid line : Bi_2O_3=1.5%
Broken line : Bi_2O_3=0%

maximum at $P=6.0$ and the values are in general, larger than those of S-system by about 1000 gauss. In Fig. 2, ${}_iH_c$ of both systems is maximum at $P=6.0$, and ${}_iH_c$ of M-system is larger than that of S-system by about 500 oersted, but this order in both systems turns over at $P>6.0$. The observed values of the same systems sintered at 1150°C are shown in Figs. 3 and 4. $4\pi I_s$ and $4\pi I_r$ are higher but ${}_iH_c$ is smaller than the values at 1100°C. And the decrease of $4\pi I_s$ in S-system at $P=6$ becomes more remarkable in this case. The curve of ${}_iH_c$ rises at $P=5.5$ in S-system and suddenly goes down at $P=6$ in M-system, as is shown in Fig. 4. The changes in $4\pi I_r$ are in general similar to those in $4\pi I_s$, but $4\pi I_r$ in M-system abruptly decreases at $P=6$ in spite of the gentle decrease of $4\pi I_s$, owing to a sudden drop of ${}_iH_c$ at this point.

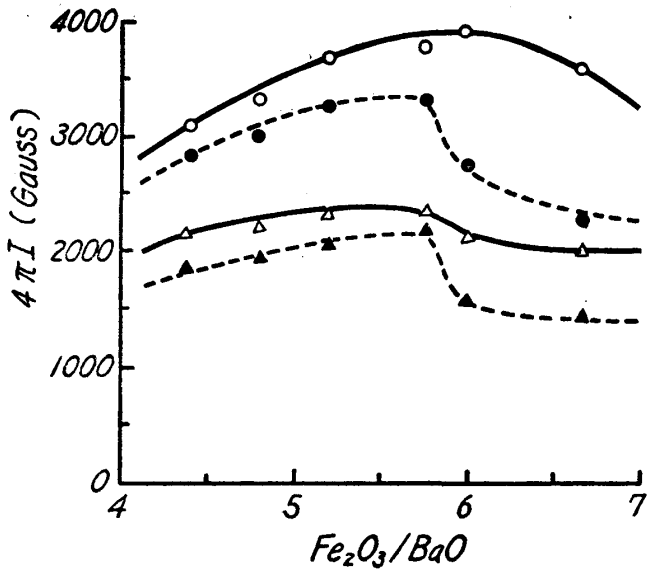

Fig. 5. Saturation and remanent as a function of Fe_2O_3/BaO for the specimens sintered at 1200°C for 15 minutes.
Solid line : $Bi_2O_3=1.5\%$
Broken line : $Bi_2O_3=0\%$

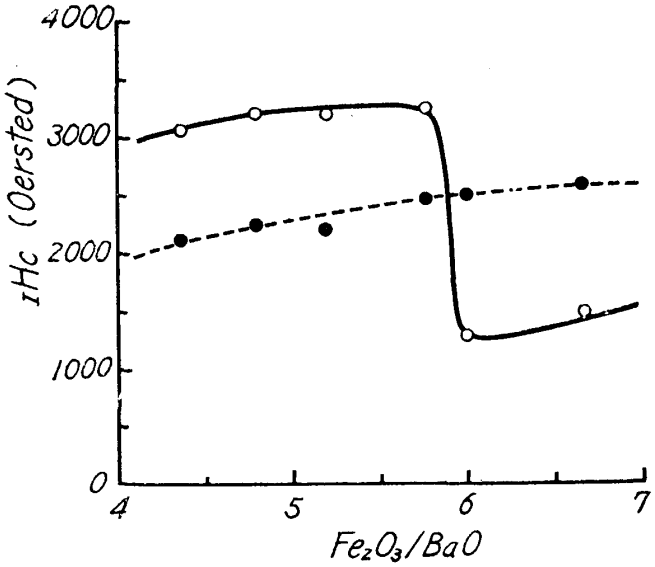

Fig. 6. Coercive force as a function of Fe_2O_3/BaO for the specimens sintered at 1200°C for 15 minutes.
Solid line : $Bi_2O_3=1.5\%$
Broken line : $Bi_2O_3=0\%$

Figs. 5 and 6 show the results obtained from the specimens sintered at 1200°C for 15 minutes. The shapes of curves in the above figures are almost the same, in spite of the difference in sintering temperature. But, differing from the curves in Fig. 2 or in Fig. 4, the steep rise of ${}_iH_c$ in S-system at $P=6$ disappears in Fig. 6.

The magnetic properties of the specimens with 2 or 2.5% Bi_2O_3, which were heated at 900°C for 2 hours and sintered at 1200°C for 15 minutes, were plotted as a function of P in Figs. 7, 8 and Figs. 9, 10, respectively.

Any significant difference could not be found between the observed values of these specimens containing less than 2.5% of Bi_2O_3.

IV. Disscussion

It has been recognized that $4\pi I_s$ and $4\pi I_r$ of $BaO\text{-}Fe_2O_3$ system increase 20~30% and ${}_iH_c$ at the composition $P<6$ increase 30~50% by the addition of 1.5% Bi_2O_3. The reason for this effect may not be made clear unless we have more experimental data. However, from the above experiments, it may be concluded as follows:

Bi_2O_3 may not have essential influence upon the magnetic properties of $BaO\cdot 6Fe_2O_3$; it may only accelerate the reaction and sintering velocity of the oxide powders. So, the specific gravity of the specimen increases by the addition of Bi_2O_3, and a higher value of $4\pi I_s$ can be obtained at lower sintering temperature. For instance, the density of *S*-system was about 4.5 under a certain sintering condition and that of *M*-system was about 5.0 at the same composition. Therefore, it is natural that the value of $4\pi I_s$ in *M*-system should increase. Some other accelerating reagents were found by the authors[5], but as a rule, the coercive force decrease by the addition of them and the property of the permanent magnet cannot be improved. On the other hand, Bi_2O_3 may improve the saturation and coercive force at the same time in the range $P<6$.

If the density were made greater than 5.0 by excessive sintering, $4\pi I_r$ and ${}_iH_c$ of $BaO\text{-}Fe_2O_3$ system would decrease abruptly, owing to grain growth as mentioned above and it was recognized by many researchers[6]. Bi_2O_3, however,

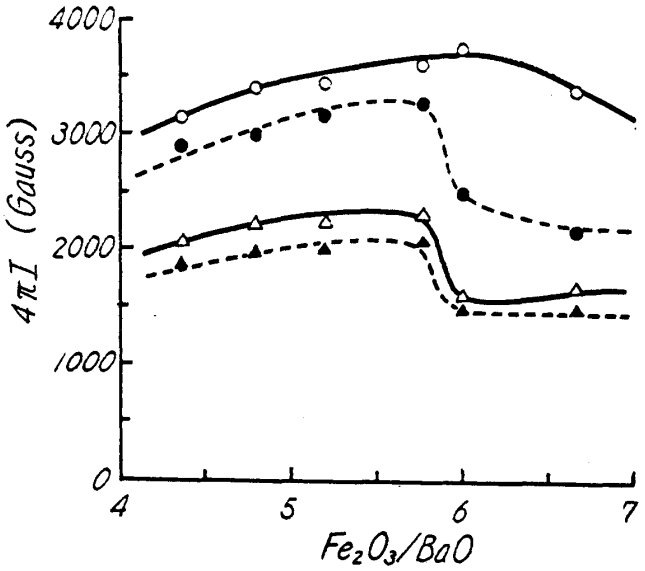

Fig. 7. Saturation and remanent as a function of Fe_2O_3/BaO for the specimens sintered at 1200°C for 15 minutes.
Solid line : $Bi_2O_3=2\%$
Broken line : $Bi_2O_3=0\%$

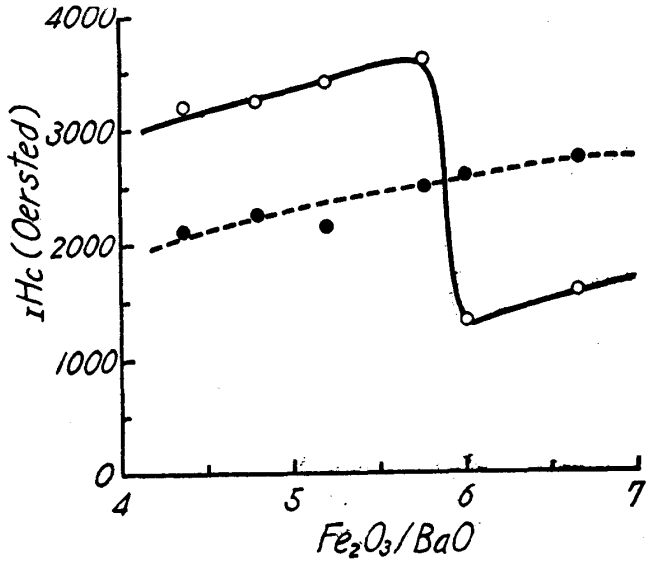

Fig. 8. Coercive force as a function of Fe_2O_3/BaO for the specimens sintered at 1200°C for 15 minutes.
Solid line : $Bi_2O_3=2\%$
Broken line : $Bi_2O_3=0\%$

(5) Ammonium chlolide, borax, etc.: T. Okamura, H. Kojima (Unpublished data)
(6) H. Hino, Toshiba Rev., 9 (1954), 866.

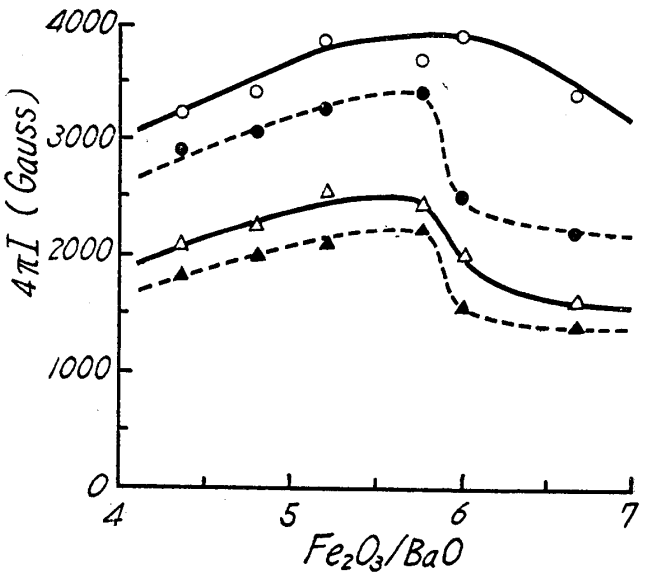

Fig. 9. Saturation and remanent as a function of Fe_2O_3/BaO for the specimens sintered at 1200°C for 15 minutes.
Solid line : $Bi_2O_3=2.5\%$
Broken line : $Bi_2O_3=0\%$

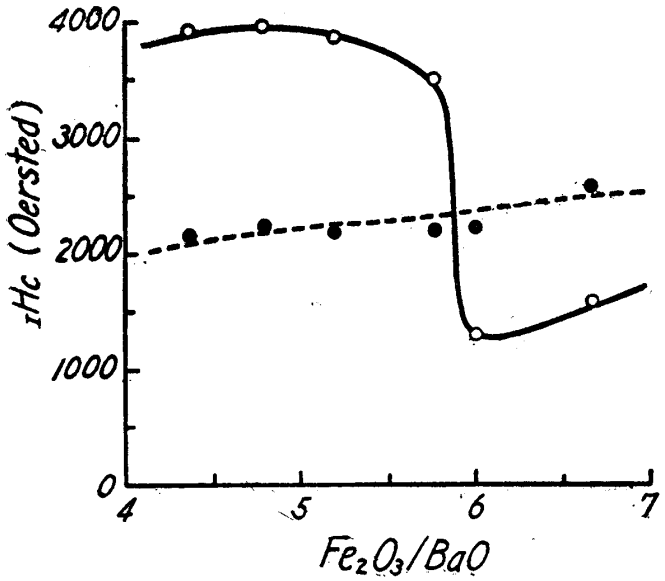

Fig. 10. Coercive force as a function of Fe_2O_3/BaO for the specimens sintered at 1200°C for 15 minutes.
Solid line : $Bi_2O_3=2.5\%$
Broken line : $Bi_2O_3=0\%$

might affect as an inhibiter of graing rowth and $_iH_c$ does not decrease in spite of the densification by it, at least, in the region $P<6.0$. The maximum observed value of $4\pi I_s$ was about 4000 gauss and the maximum point did not shift from $P=5.5$ by the addition of Bi_2O_3 in the present experiments.

The above conclusion on the effects of Bi_2O_3 is mainly based upon these experimental facts.

At any rate, it is very noteworthy from an industrial viewpoint that the magnetic and mechanical properties or producibility of BaO-Fe_2O_3 system were improved by Bi_2O_3 under the ordinary producing condition. Moreover, when Bi_2O_3 was added before sintering process, the effects were recognized to the same extent and the magnetic properties of the specimen which were improved by Bi_2O_3 and sintered under the most suitable condition, almost equal to those of the magnetically oriented magnet of similar type.

Summary

The magnetic properties were observed of Ba-ferrites with and without Bi_2O_3, changing the ratio of Fe_2O_3 and BaO from 4.4 to 6.6.

The results obtained are as follows:

(1) $4\pi I_s$ and $4\pi I_r$ of Ba-ferrite with Bi_2O_3 were larger than those of Ba-ferrite without Bi_2O_3 by 20~30% under the same producing condition.

(2) $_iH_c$ of Ba-ferrite containing Bi_2O_3 was larger than that of single Ba-ferrite by 40~50% at the composition $Fe_2O_3/BaO<6$.

(3) The above effects of Bi_2O_3 on the magnetic properties of Ba-ferrites might be not essential but due to densification.

(4) Practically, the addition of Bi_2O_3 to Ba-ferrites is very effective and their

magnetic and mechanical properties are both remarkably improved.

The study was supported partly by the grant in aid for the Fundamental Scientific Research of the Ministry of the Education. The authors wish to express their hearty thanks to Messrs. T. Fujisawa, H. Akama and C. Miyakawa for their enthusiastic assistance through the whole course of the experiments.